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The surface terminal layer and composition of the colossal magnetoresistance perovskite: La$_{0.65}$Pb$_{0.35}$MnO$_3$

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The composition in the surface region of the colossal magnetoresistance perovskite manganite materials, La$_{0.65}$A$_{0.35}$MnO$_3$ (A = Ca, Sr, Ba) has been studied using angle resolved x-ray photoemission spectroscopy. The results are consistent with a Mn–O terminal layer and Pb segregation to the near-surface region. This is similar to the behavior exhibited by La$_{0.65}$Ca$_{0.35}$MnO$_3$ and La$_{0.65}$Sr$_{0.35}$MnO$_3$. The O–Mn–O terminal layer appears to be close to the Mn$^{3+}$ valence state. © 2000 American Institute of Physics.

I. INTRODUCTION

The colossal magnetoresistance (CMR) perovskite transition metal oxides, La$_{0.65}$A$_{0.35}$MnO$_3$ (A = Ca, Sr, Ba) have been studied extensively, but the related La$_{1-x}$Pb$_x$MnO$_3$ has attracted only modest attention. $^3$-$^7$ In view of the fact that Pb will readily adopt several different valence states, unlike the alkaline earths, a comparison between the different La$_{0.65}$A$_{0.35}$MnO$_3$ (A = Ca, Sr, Ba, Pb) doping systems is important. $^3$-$^7$ Furthermore, it is possible that different dopants will affect the surface enthalpy differently $^8$-$^9$ and, consequently, the surface electronic structure and/or surface composition.

The termination layer of the perovskite manganese oxides, La$_{1-x}$A$_x$MnO$_3$ (A = Ca, Sr, Ba; $x$ = 0,0.1,0.35) has been studied using angle resolved x-ray photoemission spectroscopy, $^8$-$^{10}$ ion scattering spectroscopy, $^{11}$-$^{12}$ and angle-resolved photoemission. $^{13}$-$^{15}$ The termination layer of La$_{1-x}$A$_x$MnO$_3$, with $x$ = 0.35, has been consistently determined to be at least partly Mn–O. $^8$-$^{15}$ Unfortunately, because the surface free energy is expected to be different with the bulk, surface segregation is expected and has been routinely observed in some manganese perovskite oxides. $^8$-$^{10}$,$^{16}$,$^{17}$ This paper explores whether La$_{0.65}$Pb$_{0.35}$MnO$_3$ exhibits a similar surface composition to La$_{0.65}$A$_{0.35}$MnO$_3$ (A = Ca, Sr, Ba) thus has a similar surface free enthalpy.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The crystalline samples with a nominal thickness of 1000 Å were grown on (100) LaAlO$_3$ substrates by rf sputtering in a 4:1 argon/oxygen atmosphere at 15 mTorr with the substrate maintained at a temperature of 300 K. The films were annealed at 650 °C for 10 h and 850 °C for 2 h in an oxygen atmosphere maintained at a pressure of 1 atm (this is less annealing than used for the alkaline doped earth manganese perovskites because of lead evaporation). The bulk chemical composition of the films was determined from energy dispersive analysis of x-ray emission spectroscopy (XES or EDAX) and found to be similar to the targets with the final compositions La$_{0.65}$Pb$_{0.35}$MnO$_3$. SQUID measurements of the sample magnetization variation with temperature indicate a Curie temperature of 350 K. The crystallinity and orientation was established by x-ray diffraction. The samples were further characterized by temperature dependence magnetoresistance. The peak temperature of resistivity versus temperature curve shifted to 420 K at a 5.5 T magnetic field, and a negative relative magnetoresistance of 47% was observed at 320 K in this field. Figure 1 shows both the zero field and high field (5.5 T) resistivities (left-hand side).
The oxygen core level can provide indications of the presence of defects in the manganese perovskites. As shown in Fig. 2, the oxygen 1s core level of the perovskite manganese oxide $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$, exhibits one dominant peak at a binding energy of 529.4 eV and a shoulder at higher binding energies. This is very similar to other manganese perovskites. The higher binding energy O 1s peak found at 531.3 eV, in the perovskites, has been attributed to either a different surface oxide or to oxygen associated with defects in the perovskite structure though exact nature of the oxygen species giving rise to this 531.3 eV feature has not yet been determined. Compared to the other manganese perovskites, in $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$, this satellite feature is quite weak.

The Mn 2p spectra from the $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$ sample indicates that the disorder in the surface region is not as significant as in many other manganese perovskites. The full width at half maximum (FWHM) of the Mn 2p core level spectra is about 4 eV as compared to 4–4.5 eV for $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ and $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$. The relatively narrow Mn 2p half width is consistent with the restriction of Mn to a single valence state and an absence of significant numbers of defects in the surface region. The Mn 3p½ core level binding energies (shown in Fig. 2) of 641.5 eV for $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$ is very similar to that observed for $\text{Mn}_2\text{O}_3$ (641.6 eV) and smaller than observed for $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ (642.5 eV). The relatively narrow Mn 2p half width is consistent with the restriction of Mn to a single valence state and an absence of significant numbers of defects in the surface region. This assignment is consistent with the fact there is substantial Pb segregation (as discussed later) since Pb is allowed higher oxidation states than the generally expected alkaline earth $A^{2+}$ state ($A=\text{Ca, Sr}$) and this would act to lower the corresponding oxidation state of nearby Mn from 4+ to 3+.

The binding energy of the Pb 4f½ core level increases from 137.8 to 138.2 eV with increasing emission angle as seen in Figs. 2 and 3(b). These binding energies are greater than observed for the Pb$^{2+}$ state seen in PbTe [137.3 eV (Ref. 24)], PbS [137.5 eV (Ref. 24)], and PbO [137.4 (Ref. 25)]. Since the greater the emission angle, the more surface sensitive the x-ray photoemission signal, the higher binding energies for the Pb 4f½ at greater emission angles indicates an effectively higher oxidation of Pb in the surface region consistent with a concomitant lower oxidation of Mn in the surface region. Thus the mixed Mn$^{3+/4+}$ state of the $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ and $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ materials is suppressed in favor of a Mn$^{3+}$ state in the case of the surface region of $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$ as indicated by the core level binding energies of Pb, Mn, and by the Mn core level half width.

The XPS core level data can also be utilized to observe the surface segregation in the manganese perovskites because the effective mean free path of the escaping electrons becomes shorter with increasing emission angle. The data in Fig. 3 show the measured intensity ratio of the Pb to La core

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**III. EXPERIMENTAL RESULTS AND DISCUSSIONS**

Core level photoemission data are shown for $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$ in Fig. 2. Both the core level binding energies and peak shapes are similar to that reported previously for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_2$ by Choi et al. and Taguchi and Shimada and for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (Choi et al. and Saitoh et al.). The core level data generally suggest that the O–Mn–O layers in $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$ have fewer defects than the case for $\text{La}_{0.65}\text{A}_{0.35}\text{MnO}_3$ ($A=\text{Ca, Sr}$) consistent with the better low energy electron diffraction (LEED) pattern obtained from $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$ than is the case for $\text{La}_{0.65}\text{A}_{0.35}\text{MnO}_3$ ($A=\text{Ca, Sr}$). The LEED pattern is shown as an inset in Fig. 1 and it shows the approximate fourfold symmetry of the film’s surface.

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**FIG. 2.** The x-ray photoemission spectra of the La 3d, Pb 4f, O 1s, and Mn 2p core levels of $\text{La}_{0.65}\text{Pb}_{0.35}\text{MnO}_3$. The spectra were taken as a function of emission angle of the photoelectron and plotted as a function of binding energy.
level, which increases as a function of the increasing emission angle. Qualitatively this shows that the surface region is Pb rich. In Fig. 3(a) of are several data points taken at different temperatures averaged together. The error bars are quite small and we conclude that the surface segregation profile does not change significantly with temperature between 200 and 300 K.

IV. SUMMARY

Surface segregation in the complex oxides is relatively common and has now been identified in another manganese perovskite. The influence of the surface segregation and surface defects does appear to have some affect upon the core level binding energies and the data suggest that while L$_{α_{65}}$Pb$_{0.35}$MnO$_3$ is MnO$_2$ terminated, the Mn is in the 3+ state due to corresponding higher oxidation states of Pb in the Pb rich subsurface layer.

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